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GB 2229005 A EP 0569908 A EP 0299780 A

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## (54) Water quality measuring apparatus

(57) A sensor device for the measurement of electro-active material in water e.g Cl, comprises insulative substrate 1 e.g. of ceramic, carrying interdigitated electrodes 2, 3, a pair of electrodes 4, 5, a reference electrode 6 and conductive pads 8 - 12 to connect the device to electrical measurement apparatus. The reference electrode 6 may be partly surrounded by a screen 7. Electrodes 2, 3 are preferably microelectrodes and the conductive regions may be of noble metal or carbon. The device may be submersible for one off measurements or have water flow across it continuously. The device may be incorporated in a capillary-fill plastics vessel where the substrate forms the bottom plate of the vessel and the top plate is fixed for single use or removable for cleaning.

In use, a potential applied between electrodes 3 and 5 produces a current related to chlorine concentration, and a potential applied between electrode 2 and generator electrode 4 controls pH in the region of working electrode 3. The apparatus may also be used to measure ozone.

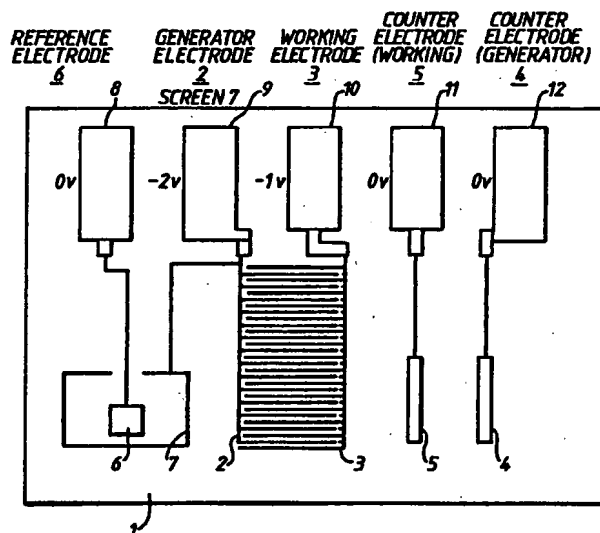


Fig. 1

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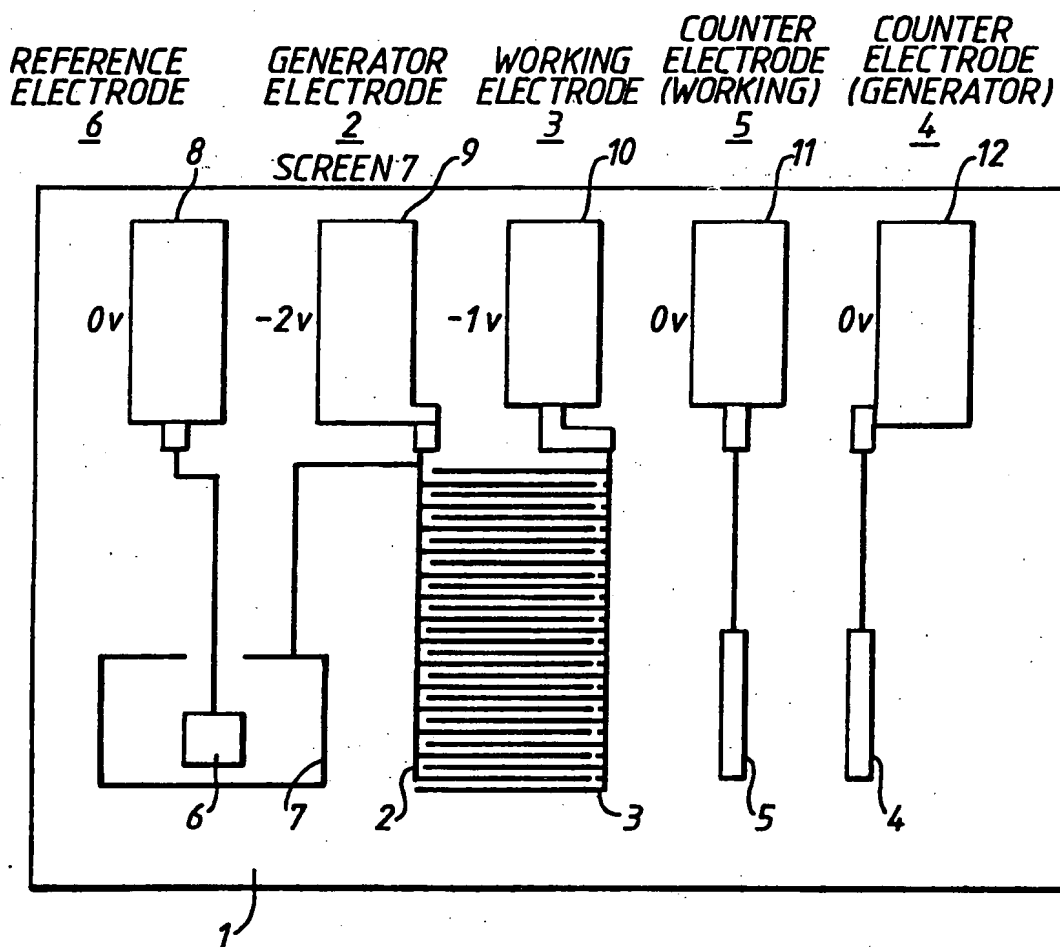
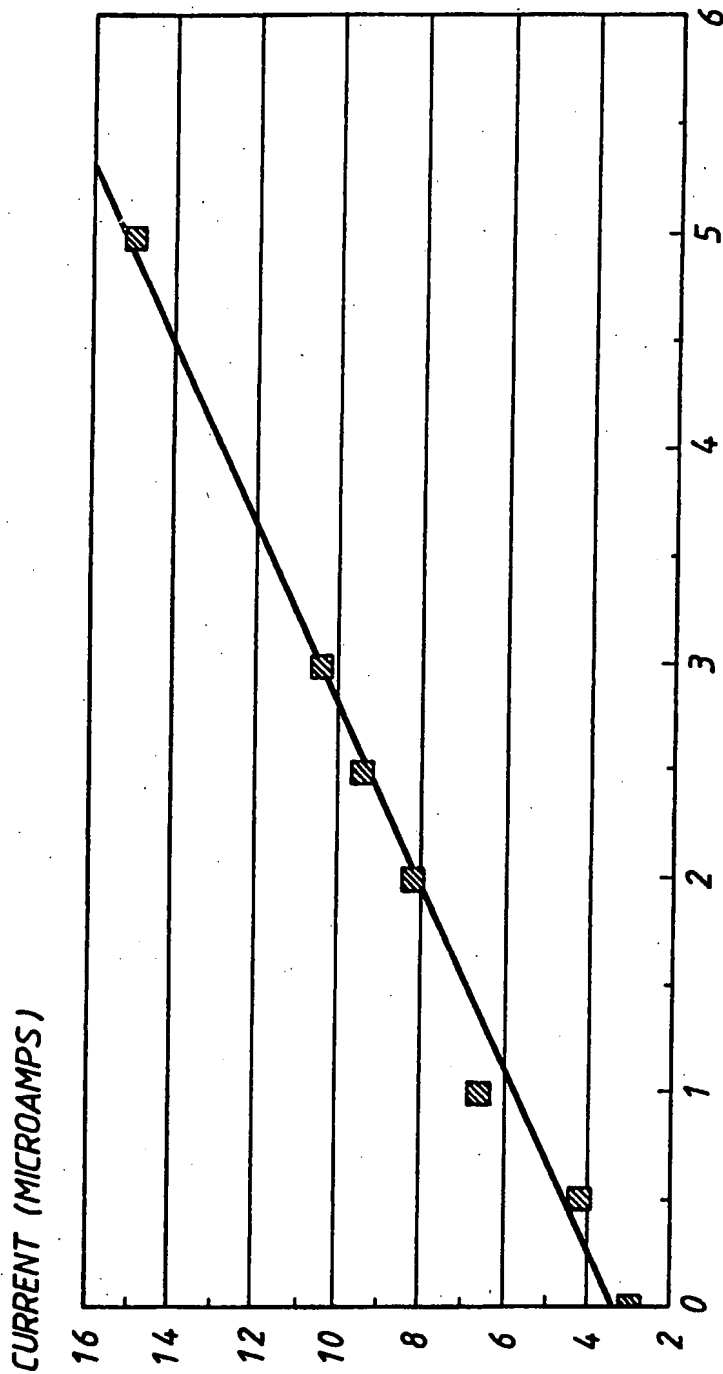


Fig. 1

CHLORINE IN WATER (pH 9)  
MICROELECTRODE ARRAY (-0.15V)



CHLORINE (PPM)

Fig. 2

## WATER QUALITY MEASURING APPARATUS

This invention relates to water quality measuring apparatus and more especially it relates to apparatus for measurement of electro-active material such as ozone or chlorine in water.

The measurement of chlorine levels in drinking water is an important need so that the level required for disinfection can be maintained within predetermined limits. There is also a requirement to monitor chlorine in swimming pools. These tests or measurements are done at present by measuring the redox potential which is an uncertain and insensitive method, or alternatively, by the use of inconvenient and inaccurate test kits.

Micro-electrodes have been used in known arrangements to measure chlorine in water with the advantage that because of the small size of the electrodes the effects of water turbulence, as may occur during continuous flow measurements, are minimised. However, micro-electrodes of the kind used in the known arrangements use very small currents which produce poor signal to noise ratios, and moreover are difficult to fabricate in a repeatable manner.

It is an object of the present invention to provide a simple robust system for the measurement of chlorine which can be the basis of continuous or single use measurements, and which provides good signal to noise ratios in use.

According to the present invention we provide for the measurement of electro-active material (such as chlorine) in water, a sensor device which in use is exposed to water to be

tested, which sensor device comprises an insulative substrate arranged to support conductive regions which define, a first pair of electrodes each having a plurality of mutually spaced fingers, wherein the fingers of one electrode are interdigitated with and spaced apart from the fingers of the other electrode, and a second pair of electrodes, and conductive pads electrically connected to each of the said electrodes, which pads serve to facilitate connection of the device to electrical measurement apparatus, and operatively associated with the device a reference electrode.

The reference electrode may be supported on the insulative substrate and defined by a part of the conductive regions.

The pairs of electrodes may be micro-electrodes.

The term micro-electrode when used herein is intended to cover electrodes of very small width, eg. about 25  $\mu\text{m}$  or less, the length being about 20 times larger than the width, or more within reasonable limits.

In use of the device a potential referenced to the reference electrode is applied between a working electrode, which is defined by one of the first pair of electrodes, and a counter electrode which is defined by one of the second pair of electrodes, to produce a current in dependence upon which chlorine concentration in the water is indicated, a further potential being applied between a generator electrode, defined by the other of the said first pair of electrodes, and a generator counter electrode, defined by the other of the said second pair of electrodes, which further potential serves to control pH in the region of the working electrode, whereby consistent and repeatable measurement is

facilitated. This controlled pH may be acid or alkaline, dependent upon the relative polarity of the generator electrodes. Thus, if the generator electrode is positive with reference to the counter generator electrode there will be an acidic environment around the generator electrode and of course vis-versa.

An important feature of the present invention is the use of a working electrode and a generator electrode having interdigitated fingers which effectively serve to provide an extended path through which measurement is made. This feature provides for relatively large operating currents and consequently greatly increased sensitivity and much better signal to noise performance when micro-electrodes are used. The provision of a device is thereby facilitated which may be simply fabricated using conventional thick film techniques, or thin film techniques using sputtering for example, and which will in use afford consistently repeatable performance.

The conductive regions may conveniently all be made of a noble metal such as palladium, platinum, or gold or alternatively they may be made of carbon or any combination of these materials.

In a case when the conductive region are all made of a noble metal or carbon or any combination of these materials, the reference electrode may comprise a region of the conductive material supported on the substrate and surrounded at least in part by an  $H^+$  or an  $OH^-$  generating structure.

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Alternatively, the reference electrode may comprise silver, or a silver halide/silver halide dielectric structure and the other electrodes may comprise platinum, gold or carbon.

In this latter arrangement, the conductive pads may also be made of platinum or alternatively they may be made from any other suitable conductive material, which may be plated to improve wear resistance and/or to minimise electrical contact resistance, with material such as gold or palladium for example.

The insulative substrate may be made of ceramic.

The reference electrode is preferably at least partly surrounded in spaced apart relationship by a screen which is supported on the substrate and connected electrically to the generator electrode.

The device may be operatively associated with measurement apparatus which provides the necessary electrical voltages and which provides an indication of chlorine level in dependence upon current flowing between the working electrode and its associated counter electrode, working a potentiostatic or in a voltammetric mode.

One embodiment of the invention will now be described by way of example only with reference to the accompanying drawings in which;

Figure 1 is a generally schematic plan view (not to scale) of a chlorine measurement device, and,

FIGURE 2 is a graph showing variation of the output of the device shown in Figure 1 with variation of chlorine concentration in water.

Referring now to the drawings, a chlorine measurement device comprises a substrate 1 made of ceramic on which are supported conductive tracks defining a pair of first electrodes 2 and 3, a pair of second electrodes 4 and 5, a reference electrode 6 and a pH generating structure 7 made of a noble metal such as platinum. As can be seen from the drawing, the pair of first electrodes, each comprise a comb like structure comprising a plurality of fingers wherein the fingers of one electrode are interdigitated symmetrically with the fingers of the other electrode. The number of fingers used may be varied according to the application but it is envisaged that up to 150 fingers may be provided on each electrode.

In use of the device as shown in the drawing, the electrodes 2 and 3 of the first pair, which are interdigitated micro-electrodes, are used respectively to define a generator electrode and a working electrode. In the present example, fingers of each electrode are 20  $\mu\text{m}$  wide and are spaced apart from the adjacent fingers of the other electrode of the pair by 20  $\mu\text{m}$ . The electrodes 4 and 5 of the second pair are used on the other hand to define counter electrodes, the electrode 4 being used as a generator counter electrode, and the electrode 5 being used as a working counter electrode. In order to apply appropriate potentials to the electrodes 2, 3, 4, 5 and 6, connection pads 8, 9, 10, 11 and 12 respectively are provided. In use of the device a voltage of about -.1 volt is applied via the pad 10 to the working electrode 3 which might be described as a potentiostatic mode of operation. Alternatively, in a voltammetric mode of operation, a potential



ramp would be applied having a start potential +.5 volts and an end potential of -.5 volts, the peak current being measured. At the same time, a voltage of about -2 volts is applied to the generator electrode 2 via the pad 9. The voltages are referenced to the corresponding counter electrodes 4 and 5 and the reference electrode which are maintained at substantially zero voltage. Chlorine concentration is indicated by means of apparatus (not shown) in dependence upon the current which flows between the working electrode 3 and its associated working counter electrode 5. The negative voltage applied between the generator electrode 2 and its associated generator counter electrode 4 is used to provide in the region of the electrodes, a controlled pH environment to facilitate consistent and accurate measurements.

In operation of the device as shown in Figure 1, variation of the output with variation in chlorine concentration, is as shown in Figure 2. It will be appreciated that conductive parts not taking part in measurements, such as submerged exposed tracks, will be insulated by means of a suitable insulative coating.

The device shown may be arranged to form a part of a submersible cell for one off measurements, or alternatively it may form a part of a measuring system wherein water is arranged continuously to flow across the electrodes to provide for continuous read outs.

A particularly convenient format for single use operation is provided by making the substrate as the bottom plate of a capillary fill device, the top plate, forming a thin layer sample cell, which may be manufactured of a plastics material formed by

injection moulding incorporating a 100  $\mu\text{m}$  step to provide the capillary gap. In operation of the capillary fill device, water to be tested is drawn between the plates by capillary attraction so that electrodes, as shown in Figure 1 of the accompanying drawings, which are carried on the bottom plate, are exposed to water to be tested. The device may be a 'single use device' which is normally thrown away after a measurement has been made or alternatively re-use may be arranged by providing a removable top plate so that the cell may be suitably cleared to facilitate re-use.

As will be apparent to those skilled in the art, with appropriate changes in the operating potential, a device as just before described may be used for the measurement of other electro-chemically oxidised or reduced species in water, such as ozone for example.

## CLAIMS

1. For the measurement of electro-active material in water, a sensor device which in use is exposed to water to be tested, which sensor device comprises an insulative substrate arranged to support conductive regions which define, a first pair of electrodes each having a plurality of mutually spaced fingers, wherein the fingers of one electrode are interdigitated with and spaced apart from the fingers of the other electrode, and a second pair of electrodes, and conductive pads electrically connected to each of the said electrodes, which pads serve to facilitate connection of the device to electrical measurement apparatus and operatively associated with the device a reference electrode.
2. A sensor device as claimed in Claim 1, wherein the reference electrode is supported on the insulative substrate and defined by a part of the conductive regions.
3. A sensor device as claimed in Claim 2, wherein the reference electrode is at least partly surrounded by a  $H^+$  or a  $OH^-$  generating structure.
4. A device as claimed in any preceding claim, wherein the first pair of electrodes are micro-electrodes.
5. A device as claimed in any preceding claim, wherein the conductive regions comprise a noble metal.

6. A device as claimed in any of Claims 1 to 4, wherein the conductive regions comprise carbon.
  7. A device as claimed in any preceding claim, wherein the insulative substrate is made of ceramic.
  8. A device as claimed in any preceding claim, operatively associated with measurement apparatus which provides the necessary electrical voltages and which provides an indication of chlorine level in dependence upon current flowing between the working electrode and its associated counter electrode.
  9. A device as claimed in any preceding claim and substantially as hereinbefore described with reference to the accompanying drawings.
  10. Apparatus including a device as claimed in any preceding claim, which in use provides a potential referenced to the reference electrode which is applied between a working electrode, which is defined by one of the first pair of electrodes, and a working counter electrode which is defined by one of the second pair of electrodes, to produce a current in dependence upon which chlorine concentration in the water is indicated, a further potential being applied between a generator electrode, defined by the other of the said first pair of electrodes, and a generator counter electrode, defined by the other of the said second pair of
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electrodes, which further potential serves to control pH in the region of the working electrode, whereby consistent and repeatable measurement is facilitated.

**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(The Search report)**

Application number  
GB 9415711.2

**Relevant Technical Fields**

- (i) UK CI (Ed.M) G1N (NBMA, NBMX, NBPE, NBPP, NBPX)  
(ii) Int CI (Ed.5) G01N (27/416, 42, 33/18)

Search Examiner  
MR J L FREEMAN

Date of completion of Search  
2 NOVEMBER 1994

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-  
1 to 10

(ii)

**Categories of documents**

- X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.
- Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X,Y	GB 2229005 A	(PLESSEY) pages 5 and 6 and Figure 1,	X: 1,4 & 5 Y: 6
Y	EP 0569908 A	(NIPPON TELEGRAPH) page 8 lines 20 to 28	6
X,Y	EP 0299780 A	(SRI INTERNATIONAL) page 2 lines 42 to 48 and Figure 3	X: 1,4 & 5 Y: 6

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).